Laboratory evidence for a key intermediate in the Venus atmosphere: Peroxychloroformyl radical

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For two decades, the peroxychloroformyl radical, ClC(O)OO, has played a central role in models of the chemical stability of the Venus atmosphere. No confirmation, however, has been possible in the absence of laboratory measurements for ClC(O)OO. We report the isolation of ClC(O)OO in a cryogenic matrix and its infrared and ultraviolet spectral signatures. These experiments show that ClC(O)OO is thermally and photolytically stable in the Venus atmosphere. These experimental discoveries validate the existence of ClC(O)OO, confirm several longstanding model assumptions, and provide a basis for the astronomical search for this important radical species.

The chemical composition of the atmosphere of Venus has been analyzed by using ground-based and space-probe observations. These studies have shown that the atmosphere of Venus is composed primarily of CO_2, a small amount of N_2, and trace abundances of CO, H_2O, HCl, and SO_2 (1). The central problem in Venus atmospheric chemistry is the remarkable stability of CO_2 despite its dissociation to CO and O_2 by the absorption of solar ultraviolet (UV) radiation. Several investigations have examined the role of chlorine in the catalytic recombination of CO and O_2 (2–4). One proposed oxidation mechanism (4) involved the chloroformyl radical, ClCO, which was shown later to have a lesser role (5, 6). An alternative mechanism for the catalytic oxidation of CO to CO_2 utilizes the peroxychloroformyl radical, ClC(O)OO, as the key reactive agent (6). Inclusion of this chemistry provides an explanation for the low CO and O_2 concentrations in the Venus atmosphere. However, despite its suggested central role in Venus chemistry, ClC(O)OO has been experimentally elusive. Here, we report the laboratory isolation of ClC(O)OO, allowing an examination of its stability at Venus middle-atmospheric temperatures, measurements of its infrared (IR) and UV spectra in low-temperature matrices, and finally, consideration of the implications of these laboratory results for Venus chemistry.

Isolation of ClC(O)OO

The radical ClC(O)OO was prepared from pure $ClC(O)OONO_2$. The latter species was detected originally in low concentrations in a gas-flow system (7) but was synthesized for the present investigation. In separate experiments, ClC(O)OO was generated by means of thermal decomposition of $ClC(O)OONO_2$ with the products trapped in frozen matrices or by photolysis of a mixture of CO/Cl_2 in O_2 ice matrices. In either case, the resultant ice matrices were analyzed spectroscopically.

Details of the matrix apparatus are given elsewhere (8, 9). Pyrolysis occurs in a quartz tube with a pinhole 1 mm in diameter at the end of the tube. This tube (the spray-on nozzle) is placed in high vacuum 2 cm in front of the cold matrix support. Ice spectra are recorded by using a Bruker (Billerica, MA) 66v Fourier-transform IR spectrometer in the reflectance mode, with transfer optics from 5,000 to 400 cm^{-1} and a spectral resolution of 1 or 0.25 cm^{-1}. A deutero-triglycinsulfate detector and KBr/Ge beam splitter are used. For these experiments, 64 scans were coadded for each spectrum. The UV spectrum is measured in reflectance with a Perkin–Elmer Lambda 900 UV spectrometer with a 1-nm resolution using two quartz optical fibers and special condenser optics.

In the thermolysis experiments, ClC(O)OO was formed in flowing mixtures of $ClC(O)OONO_2$/Ar or Ne heated at 200, 250, 300, 350, 400, and 450°C:

$$ClC(O)OONO_2 \xrightarrow{\Delta} ClC(O)OO + NO_2. \qquad [1]$$

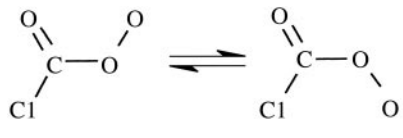
ClC(O)OO also was produced by photolysis at $\lambda > 305$ nm of a frozen composition of $Cl_2/CO/O_2$ in a ratio of 1:20:400. The formation of ClC(O)OO results from the following reaction sequence:

$$\begin{aligned} Cl_2 + h\nu &\rightarrow 2Cl \\ Cl + CO &\rightarrow ClCO \\ ClCO + O_2 &\rightarrow ClC(O)OO. \end{aligned} \qquad [2]$$

Fig. 1 compares the IR matrix spectrum of the starting material $ClC(O)OONO_2$ (Fig. 1*A*), resulting from photolysis of the $CO/Cl_2/O_2$ ice mixture (Fig. 1*B*) thermolysis of $ClC(O)OONO_2$ at 250°C (Fig. 1*C*). There are common features in Figs. 1 *B* and *C* that are not shown in Fig. 1*A*, which are attributed to the ClC(O)OO radical. As expected from Eq. **1**, the other expected thermolysis product, NO_2, is trapped and is clearly in evidence in the spectrum shown in Fig. 1*C*. The thermolysis and photolysis results are consistent with previous work suggesting the existence of ClC(O)OO [(*i*) thermolysis of $ClC(O)OONO_2$ yielding NO_2 and CO_2 (7) and (*ii*) measurements of the oxidation of ClCO by O_2 (7, 10)], but the existence of ClC(O)OO had not been demonstrated explicitly.

Spectroscopy

The ClC(O)OO radical has as its ground state the $\hat{x}\ ^2A''$ electronic configuration. There are two rotamers for the ClC(O)OO radical: cis and trans conformations defined by the ClCOO dihedral angle.



[3]

Abbreviations: CCSD(T), single and double excitation-coupled cluster with a perturbation estimate of triple excitations; aug-cc-pVDZ, Dunning augmented correlation consistent basis set.

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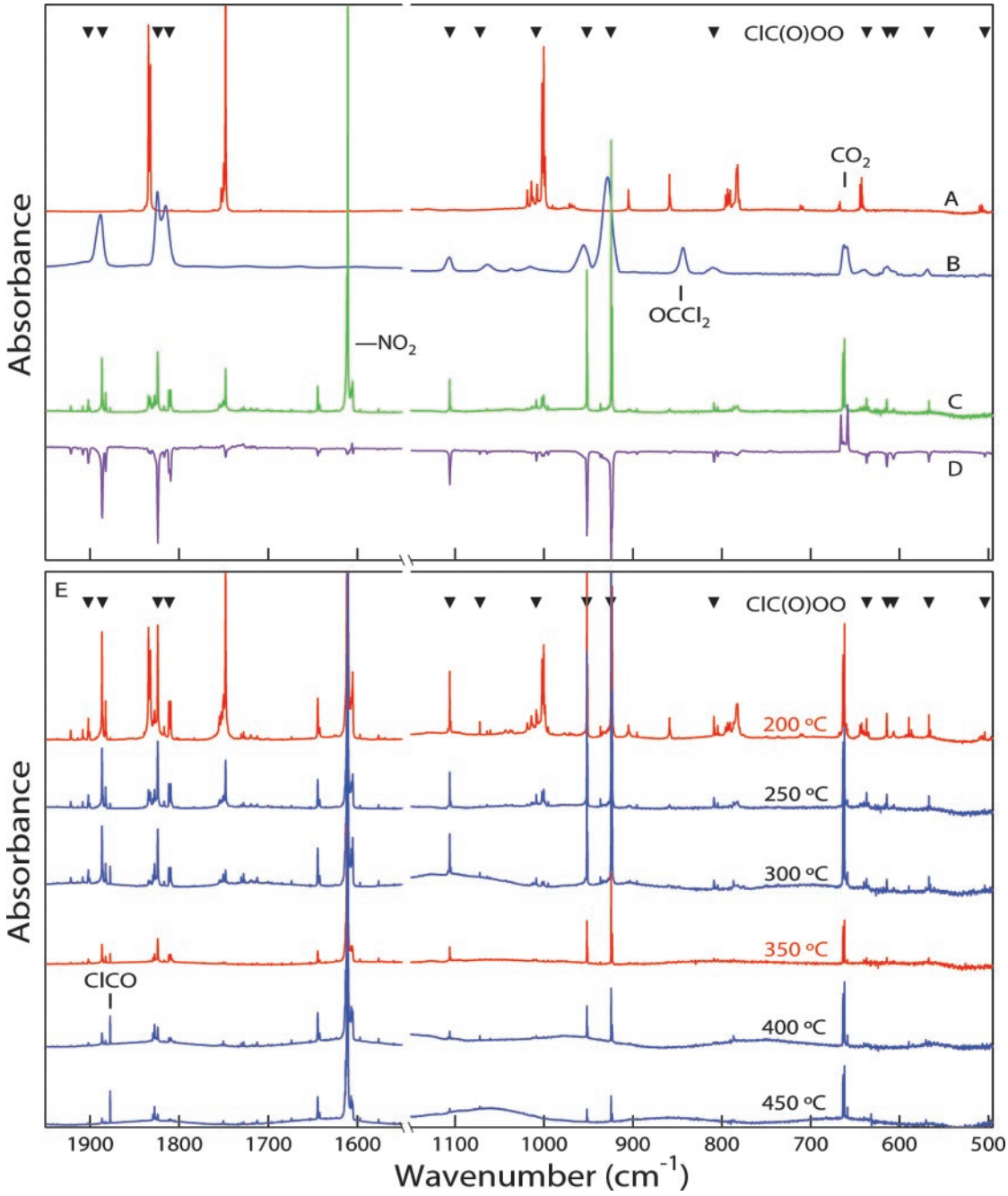

Fig. 1. IR spectra of $ClC(O)OONO_2$ and products in frozen matrices. IR spectra of $ClC(O)OONO_2$ isolated in an argon matrix (*A*), Cl_2/CO mixture in an O_2 matrix (relative abundances 1:20:400) after 15 min of irradiation at $\lambda > 305$ nm (*B*), and thermolysis products of $ClC(O)OONO_2$ at 250°C isolated in an argon matrix (*C*). The positions of the ClC(O)OO features tabulated in Table 1 are indicated; they are not present in *A* but are clearly present in both *B* and *C*. (*D*) The difference spectrum of *C* and the resultant IR spectrum after 30 min of photolysis at $\lambda = 255$ nm. Note that the ClC(O)OO features are negative in the difference spectrum, indicating that they have decreased in intensity as a result of the photolysis. (*E*) IR spectra of thermolysis products of $ClC(O)OONO_2$ at 200, 250, 300, 350, 400, and 450°C isolated in an argon matrix. Because the thermal dissociation threshold for $ClC(O)OONO_2$ is ≈200°C, the ClC(O)OO abundance is largest in the 200°C experiment. When the temperature increases to >350°C, ClC(O)OO thermally decomposes and ClCO features appear in these spectra.

Vibrational spectra were calculated theoretically by using the single and double excitation-coupled cluster with a perturbation estimate of triple excitations [CCSD(T)] theory (11) based on unrestricted Hartree–Fock wavefunctions. Structures of the local minima were fully optimized by using the Dunning augmented correlation-consistent basis set (aug-cc-pVDZ) (12). The optimized geometries for *trans*-ClC(O)OO and *cis*-ClC(O)OO are as follows: CCSD(T)/aug-cc-pVDZ optimized geometry for *trans*-ClC(O)OO is r(C—Cl) = 1.747 Å, r(C═O) = 1.188 Å, r(C—O) = 1.434 Å, r(O—O) = 1.344 Å, θ(O═C—O) = 126.5°, θ(ClC═O) = 127.7°, θ(COO) = 110.4°, and τ(ClCOO) = 180.0°; and CCSD(T)/aug-cc-pVDZ optimized geometry for *cis*-ClC(O)OO is r(C—Cl) = 1.741 Å, r(C═O) = 1.192 Å, r(C—O) = 1.438 Å, r(O—O) = 1.337 Å, θ(O═C—O) = 117.8°, θ(ClC═O) = 127.0°, θ(COO) = 114.8°, and τ(ClCOO) = 0.0°.

The observed vibrational band positions and band intensities for ClC(O)OO obtained by thermolysis of $ClC(O)OONO_2$ and quenched in an argon matrix are given in Table 1. For compar-

Table 1. IR band positions and intensities of ^{35}ClC(O)OO isolated in an argon matrix

trans-ClC(O)OO		*cis*-ClC(O)OO			
Experiment*	Theory†	Experiment*	Theory†	Assignment	Mode
—	—	1,902 (8.8)	—	$2\nu_3$	—
1,886 (60)	1,864 (80)	1,824 (55)	1,843 (87)	ν_1(a′)	ν(C=O)
1,811 (26)	—	—	—	$2\nu_3$	—
1,072 (2.6)	1,047 (1)	1,106 (17)	1,093 (14)	ν_2(a′)	ν(O–O)
1,009 (12)	—	—	—	$2\nu_5$	—
925 (100)	938 (100)	952 (37)	963 (69)	ν_3(a′)	ν(C–O)
809 (7.4)	803 (9)	637 (5.6)	633 (6)	ν_4(a′)	ν(C–Cl)
614 (5.7)	609 (3)	607 (3.5)	603 (4)	ν_8(a″)	γ(ClCOO$_2$)
504 (0.9)	498 (2)	567 (6.0)	569 (7)	ν_5(a′)	δ(Cl–C=O)
—	401 (0.6)	—	462 (0.1)	ν_6(a′)	δ(O–C=O)
—	288 (0.3)	—	279 (0.5)	ν_7(a′)	δ(O–C–Cl)
—	134 (0.017)	—	116 (0.2)	ν_9(a″)	τ

*Frequencies are in units of cm^{-1}; relative intensities are presented in parentheses.
†Frequencies are in units of cm^{-1} were calculated at the CCSD(T)/aug-cc-pVDZ level of theory. The relative intensities (in parentheses) were calculated at the Becke three-parameter functional/aug-cc-pVDZ level of theory. The relative intensity of 100 was assigned to the absolute intensity 402.8 km·mol^{-1}.

ison, vibrational frequencies for the CCSD(T) level of theory calculated numerically by using the above geometries are also shown. To check the consistency and reliability of these results, an independent calculation using density functional theory with the Becke three-parameter functional method (13) was used with the aug-cc-pVDZ basis set. All bands belonging to the cis or trans species are easily assigned by comparison with the predicted IR *ab initio* calculation results. In the 1,850 cm^{-1} region, the deviations from the predictions are not satisfying, because the ν(C═O) bands are disturbed by Fermi resonances with the $2\nu_3$ band. Note that the ratio of the observed summed relative intensities reported in Table 1 for cis/trans is ≈0.6, which is close to the thermodynamic equilibrium value of ≈0.7 at 250°C expected because the relative energy of the trans rotamer is ≈1.5 kJ·mol^{-1} below that of the cis rotamer.

Additional evidence for the identification of ClC(O)OO comes from isotope-substitution experiments. For *cis*-ClC(O)OO produced by photolysis in an $^{18}O_2$ matrix, the bands at 1,106, 952, 637, and 567 cm^{-1} are shifted to lower wavenumbers by 52, 16, 10, and 19 cm^{-1}, respectively. The first three measured shifts are consistent in magnitude and sign with the predicted shifts (14) for the assignment of those bands attributed to the O—O, C—O, and C—Cl stretch vibrations of *cis*-ClC(O)OO, respectively.

The UV spectrum of the thermolysis-produced matrix-isolated products is shown in Fig. 2. In this spectrum, the ClC(O)OO radical is a strong absorber around 230 nm. Photolysis of the matrix at λ = 255 nm results in the simultaneous decrease of all ClC(O)OO IR bands and an increase in CO_2 IR bands (Fig. 1*D*). In addition, the resultant UV spectrum shows a decrease in the 230-nm band and the appearance of a band due to ClO, which suggests that the photodissociation of ClC(O)OO results in the elimination of ClO:

$$\mathrm{ClC(O)OO} \xrightarrow[255\ \mathrm{nm}]{h\nu} \mathrm{CO_2} + \mathrm{ClO}. \qquad [4]$$

Although the dissociation limit of the ground electronic state of ClC(O)OO favors formation of ClCO and O_2, the above result shows that excited-state photochemistry does not mimic necessarily the ground state, nor is the ground state structure a good predictor of excited-state photochemistry.

Thermal Stability of ClC(O)OO

Fig. 1*E* shows the IR spectra from all the thermolysis experiments. The matrix abundance of ClC(O)OO is largest in the 200°C experiment, which is consistent with the threshold of 115 ± 3.2 kJ·mol^{-1} (15) for dissociation of ClC(O)OONO$_2$ yielding ClC(O)OO. Note that some CO_2 also can result from the self-reaction of ClC(O)OO. At and above a thermolysis temperature of ≈350°C, the matrix abundance of ClC(O)OO is seen to decrease, and secondary dissociation into ClCO [reported IR spectra (16)] and O_2 is observed. Because the dissociation threshold for the ClC(O)—OO bond is higher than the threshold for the ClC(O)OO—NO$_2$ bond by a factor of ≈1.5, the bond energy for ClC(O)OO dissociation should be ≈169 kJ·mol^{-1}.

Implications for Venus Chemistry

These experimental results provide important confirmations for assumptions adopted in Venus chemistry simulations for more than two decades. To explain the stability of the CO_2 atmosphere and reproduce the observed O_2 observations, chemical reactions involving ClC(O)OO were proposed (6, 17). The inclusion of ClC(O)OO chemistry reduces the model prediction for the O_2

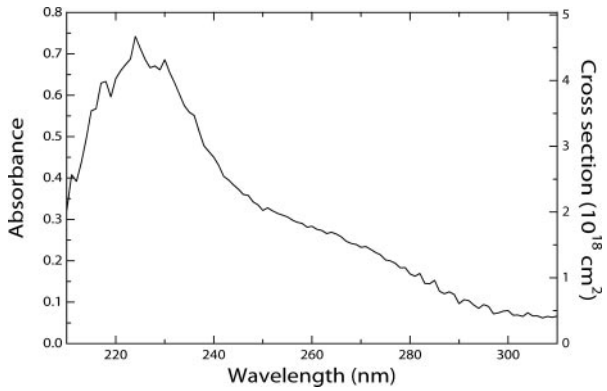

Fig. 2. The UV spectrum of the thermolysis products of ClC(O)OONO$_2$ at 250°C isolated in a Ne matrix. Computation of a cross section from absorbance is based on an assumption that the yield for FC(O)OO and ClC(O)OO from thermal decomposition of FC(O)OONO$_2$ and ClC(O)OONO$_2$, respectively, is the same under similar experimental circumstances and that the conversion of absorbance to cross section in the FC(O)OO matrix measurements (24) is applicable to the ClC(O)OO matrix measurements.

Table 2. Comparison of Venus observation of column O_2 abundance with model simulations

Result	Column O_2,* molecules per cm^2
Observation (18)	$<1.5 \times 10^{18}$
Model† without ClC(O)OO included	3.05×10^{19}
Model† with ClC(O)OO kinetic reactions	2.14×10^{18}
Model† with ClC(O)OO photolysis and kinetic reactions	2.13×10^{18}

*Integrated from 58-km altitude to top of atmosphere.
†Described in ref. 17.

column density from 3×10^{19} to 2×10^{18} cm^{-2} (17), the latter closely approximating the observational upper limit of $<1.5 \times 10^{18}$ cm^{-2} (18, 19) (see Table 2 for summary). Previous model work (20) predicted a smaller O_2 column abundance ($<1.5 \times 10^{18}$ cm^{-2}), assuming that CO oxidation occurs primarily by $ClCO + O_2 \rightarrow CO_2 + ClO$ as proposed (21). More recent measurements (22) suggest, however, that ClCO is much less stable than what seems to have been assumed in ref. 20, which would reduce the rate of CO oxidation through this channel and increase the predicted O_2 abundance in the absence of another mechanism [such as reactions involving ClC(O)OO]. In light of existing uncertainties in the interpretation of the available Venus O_2 observations (19), a definitive confirmation of the CO oxidation mechanism also awaits more precise measurements of the total abundance and altitude distribution of O_2 above the cloud tops.

In the earlier models (6, 17), ClC(O)OO was assumed to be stable at Venus middle-atmospheric temperatures of −100 to 0°C, and no thermal dissociation reactions were included in the simulations. The experimental results reported here that the threshold for ClC(O)OO thermal decomposition is 350°C validates this critical model assumption.

In the absence of any laboratory measurements of UV cross sections, previous models also did not include ClC(O)OO photodissociation. A recent Venus photochemical simulation (the "one-sigma" model described in ref. 17) was updated to include ClC(O)OO photodissociation using the UV cross sections of Fig. 2. The California Institute of Technology/Jet Propulsion Laboratory photochemical model (23) was used in its one-dimensional mode. Photodissociation rates were calculated for local noon at 45° latitude and then divided by two to simulate global average conditions between 58 and 112 km in altitude. Because the primary products of UV photolysis of ClC(O)OO are ClO and CO_2, as discussed above, the inclusion in a model of ClC(O)OO UV photolysis based on the spectrum shown in Fig. 2 results in only minor changes in model results for the CO_2-reformation rate and the O_2 column density. [The abundance of, and the rate of reformation of CO_2 through, ClC(O)OO are primarily controlled kinetically, although reformation of CO_2 through ClC(O)OO photolysis is not negligible.]

Summary

Essential features of current models accounting for the chemical stability of the Venus atmosphere are now supported by laboratory experiments. To complete a satisfactory understanding of Venus middle-atmosphere chemistry, what is needed is direct detection of key reactive-species abundances consistent with the predictions of the model simulations. The IR spectrum of ClC(O)OO reported herein will allow a search for this central species. In addition, precise measurements of O_2 distribution above the cloud tops are needed.

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